Superlow friction behavior of diamond-like carbon coatings: Time and speed effects

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(Received 6 November 2000; accepted for publication 28 February 2001)

The friction behavior of a diamond-like carbon coating was studied in reciprocating sliding contact at speeds from 0.01 to 5 mm/s, in dry nitrogen. ''Superlow'' friction coefficients of 0.003–0.008 were obtained in continuous sliding at the higher speeds (>1 mm/s). However, friction coefficients rose to values typical of diamond-like carbon in dry and ambient air (0.01–0.1) at lower speeds (<0.5 mm/s) as well as in time-delayed, higher speed tests. The rise of the friction coefficients in both speed and time-delay tests was in good quantitative agreement with gas adsorption kinetics predicted by the Elovich equation for adsorption onto carbon. More generally, superlow friction could be sustained, suppressed, and recovered as a function of exposure time, demonstrating that duty cycle cannot be ignored when predicting performance of superlow friction coatings in devices.
 [DOI: 10.1063/1.1366649]

The past 10 years has seen a steady lowering of the friction coefficient thanks to innovations in applied surface science and coating technology. Friction coefficients below 0.01 have been observed for certain MoS_2 and diamond-like carbon (DLC) coatings, but only in ultrahigh vacuum.[1–3] Coatings with friction coefficients in this range can eliminate the need for liquid lubrication and enable new classes of sliding devices. However, friction coefficient is not a materials parameter; rather, it depends on factors like contact stress, sliding speed, environment, and tribochemical properties of the sliding interface.[4–6] For example, it is known that the friction of graphite in vacuum is reduced by exposure to O_2 or H_2O,[7] while for DLC, exposure to these gases increases friction.[8,9] Moreover, conditions for maintaining low friction coefficients are not very well understood, and what works in one application may be useless in another. Thus, the success of DLC in the hard disk industry as a protective, friction reducing coating, for example, has not been readily translated to microelectromechanical or pointing-and-tracking devices, where operating conditions such as speed and environment are vastly different.

In this letter we introduce a methodology for assessing the friction behavior of coatings for low speed sliding applications. DLC coatings that give friction coefficients down to 0.001 at atmospheric pressure in dry nitrogen were investigated.[10,11] By systematically varying speed and environmental exposure times, superlow friction could be sustained or lost, but always recovered. The friction behavior is explained in terms of gas adsorption.

DLC coatings were prepared by low temperature, plasma assisted chemical vapor deposition in a hydrogen and hydrocarbon rich environment.[11] Coatings were deposited to 1 μm thickness on 6.35 mm diameter sapphire balls, 12.7 mm diameter steel balls, and on H13 steel flats. Friction tests were performed with a reciprocating, ball-on-flat tribometer in a nominally dry nitrogen environment (RH$\leqslant$1%, O_2<1%).[12] The coated ball was loaded against the coated flat to 9.8 N (0.6–1.1 GPa Hertzian mean pressure) and slid at speeds ranging from 10 to 5000 μm/s. Each track was initially run-in for 1000 cycles at sliding speeds $\geqslant$1000 μm/s. The length of the track was 5.0 mm. The friction coefficient was averaged over each cycle, excluding contributions from the endpoints.

The effect of exposure time on friction was first studied as a function of speed. A series of ''speed-dependent'' tests was performed on a run-in track. Each speed test began with 100 cycles at high speed (1–5 mm/s) followed by 20 cycles at a lower speed (10–513 μm/s). The ball remained in contact with the flat, and sliding continued with no delays throughout the series.

The friction behavior of one of the DLC couples for a series containing seven different speed-dependent tests is shown in Fig. 1. The friction coefficient fell to a superlow value of 0.007 during the high speed portion of each test. However, at lower speeds ($\leqslant$513 μm/s), the friction coefficient increased to values from 0.01 to 0.1 as the speed decreased. No obvious wear could be seen in Nomarski optical microscopy of the ''wear'' track on the ball or flat after tests like that of Fig. 1. Similar tests were performed on over 30 tracks of this couple and on 15 tracks on three other couples. Overall, run-in friction coefficients ranged from 0.003 to 0.008, consistent with results of Erdemir *et al.*,[11] and friction behaviors similar to that shown in Fig. 1 were obtained, independent of the order in which the speed tests were performed.

The low speed friction data of Fig. 1 have been replotted as a function of reinitialized cycle number in Fig. 2 so that the rates of frictional increase can be easily compared between different speeds. The friction coefficient increased more rapidly and saturated sooner at the lower speeds. At the lowest speed, 10 μm/s, the rate of increase dropped to zero

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Report Documentation Page	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
2001		**00-00-2001 to 00-00-2001**

4. TITLE AND SUBTITLE **Superlow friction behavior of diamond-like carbon coatings: Time and speed effects**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Research Laboratory,Code 6176,4555 Overlook Avenue, SW,Washington,DC,20375**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S)
	11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**		**3**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

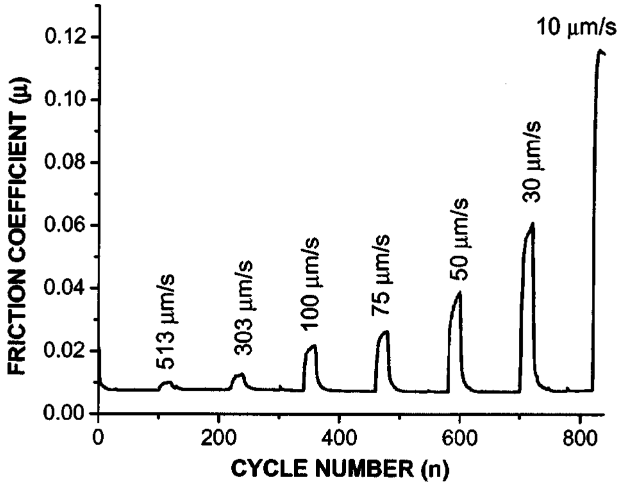

FIG. 1. Friction coefficient vs cycle number from a speed-dependent test at seven speeds.

after eight cycles and the friction coefficient saturated at 0.12. This value is typical of DLC coatings in ambient air[13] and $\sim$20 times higher than the run-in value of 0.007.

Although Fig. 2 might suggest that the friction coefficient depended directly on speed, an alternative interpretation is that speed influenced friction indirectly by changing the length of time that points along the track were exposed to environmental gases. To distinguish between these two possibilities, a second series of tests was performed in which the exposure time was varied but the sliding speed remained constant. These ''time-delay'' tests were like the speed-dependent tests in that 100 cycles at high speed ($\geqslant$1 mm/s) were followed by 20 cycles of varying exposure time. However, in this case the exposure time was not established by speed but rather by introducing fixed delays at the endpoints of the track, then sliding at high speed along the track for all tests. Delays were chosen such that the average exposure time per cycle was equal to the traverse time in the speed tests. As in the speed tests, a series of time delays was studied without breaking contact between the ball and the flat.

Results from a series of five different time-delay tests on a different track are shown in Fig. 3 plotted as a function of reinitialized cycle number. Even though the speed was constant, the friction coefficient increased as the exposure time increased. The similarity of these data to those plotted in Fig. 2 shows that the increase in friction was governed by exposure time and not by speed. In both cases exposure time had to be greater than about 5 s for the friction to increase. Small deviations between the time-delay and speed-dependent data do exist but are beyond the scope of this letter.

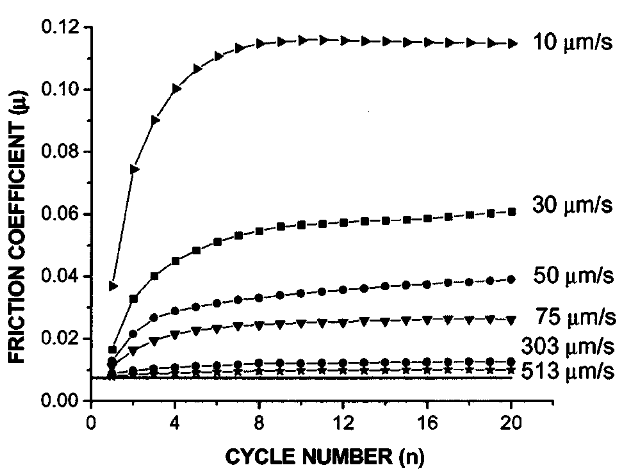

FIG. 2. Friction coefficient vs reinitialized cycle number taken from low speed data in Fig. 1. The solid line indicates the high speed friction coefficient: $\mu=0.007$.

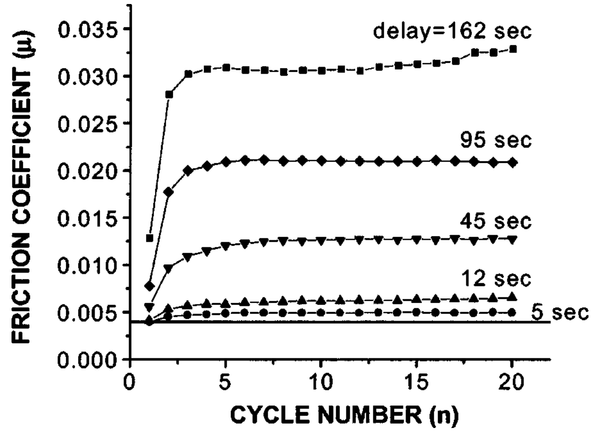

FIG. 3. Friction coefficient vs reinitialized cycle number for five different time-delay tests. The solid line indicates the high speed friction coefficient for this DLC couple: $\mu=0.004$.

The increase of the friction coefficient with exposure time can be interpreted in terms of gas interactions with the track. Zaïdi *et al.*[14] provided a basis for interpretation in somewhat similar studies of the friction behavior of graphite in a vacuum chamber. They found that the steady-state friction coefficient fell as the partial pressure of O_2 increased or the speed decreased. (We note that in their experiment, the O_2 gas reduced the friction coefficient, whereas in ours, gas appeared to have increased the friction coefficient.) They invoked the Elovich equation,[15–17] which describes the kinetics of adsorption of O_2 on charcoal, to show that exposure time was common to both speed and partial pressure behaviors.

In our interpretation, each time the ball passes a point on the track, it wipes the track and re-exposes it to gases in the environment. According to the Elovich equation, the rate of adsorption is exponentially proportional to the amount adsorbed at the surface

$$\frac{dq}{dt}=Ae^{\alpha q}, \tag{1}$$

where q is the normalized amount of adsorbate, A is a constant related to the particle flux, and α is a constant associated with the number of available adsorption sites. Equation (1) can be related to the time evolution of average friction through two steps.[14] First by integration of Eq. (1) over a period, T, and then by assuming that the friction is proportional to the amount of gas adsorbed, $\mu\propto q$:

$$\mu(T)=\mu_0+\frac{\mu_1-\mu_0}{\alpha}\ln(1+A\alpha T), \tag{2}$$

where μ_0 is the initial friction coefficient, and μ_1 is the final friction coefficient.

Data from Fig. 2 are replotted (open symbols) as a logarithmic function of time in Fig. 4. The solid lines are fits of the data to Eq. (2) using a single set of A and α values: A

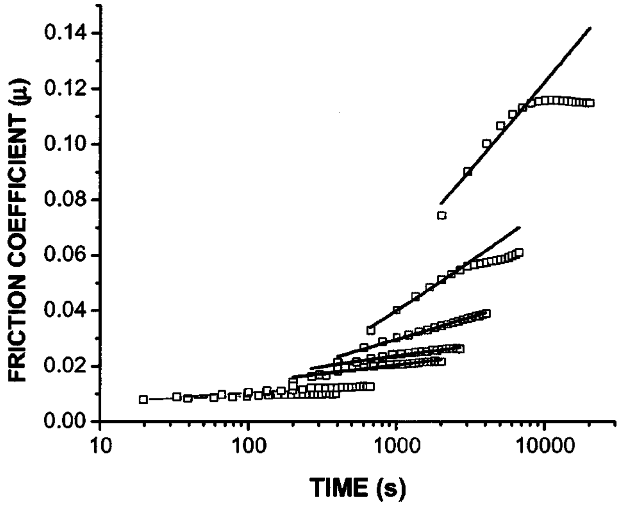

FIG. 4. Friction coefficient data from Fig. 2 replotted as a function of time (open symbols). Fit of Eq. (2) to the data (solid lines). Two constants, $A=3.40$ and $\alpha=0.75$, fit the entire data set.

$=3.4\,s^{-1}$ and $\alpha=0.75$. In addition, Eq. (2) has been applied to several other data sets. The resulting fits were universal within an individual series of tests although the values of A and α between series differed; values for A ranged from 0.48 to 3.4 s^{-1} and values for α ranged from 0.23 to 2.1. The equation gave an excellent fit of the initial rise in friction at each speed in Fig. 4, suggesting that gas-surface interactions were responsible for the increased friction. However, the Elovich equation failed to account for the leveling out of the friction coefficient at the lowest speeds. The Langmuir equation,[18] which also can be used to describe gas adsorption kinetics, includes a saturation term. It could be fit to the data of Fig. 4 (not shown), but only by adjusting the Langmuir parameters for each speed test (i.e., the fit was not universal). A more complete model of the friction behavior would include both gas adsorption and removal (through wiping) terms.

In summary, we have shown that these DLC coatings could sustain superlow friction coefficients (0.003–0.008) in nominally dry N_2, so long as the exposure time between sliding contacts remained below about 5 s. Longer exposures caused the friction coefficient to increase to values normally associated with typical DLC coatings in ambient air, but the superlow friction coefficient was recovered by reducing the exposure time below the nominal value. Finally, the excellent fit of the time-dependent friction behavior to the Elovich equation indicates that gas-surface interactions play a strong role in inhibiting superlow friction.

The authors thank Mike Dugger for loaning us an oxygen sensor, John Russell, Jr. and Steve Harris for valuable discussions. J.A.H. was supported by an ASEE postdoctoral associateship. Funding for this project was provided by the Office of Naval Research and Department of Energy, Office of Energy Research (Contract No. W-31-109-Eng-38).

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